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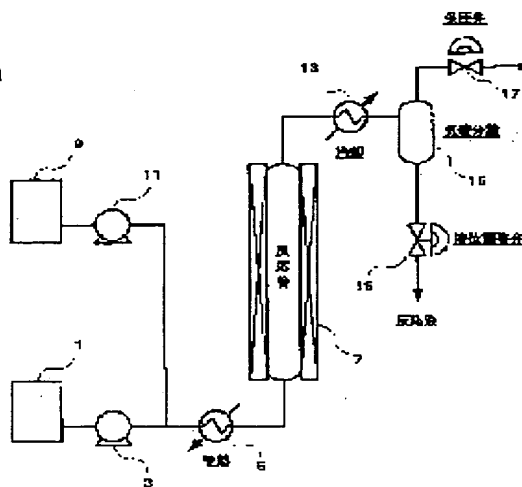
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(54) MANUFACTURING METHOD OF FUEL GAS

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a new technology with which solid and liquid organic wastes are recovered in the form of fuel gas, electricity and thermal energy for reutilization by treating the organic waste at a high gasification efficiency.

SOLUTION: A manufacturing method of a fuel gas containing hydrogen as a principal component comprises hydrothermal reacting a liquid organic material in supercritical water in a reactor.



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CLAIMS

[Claim(s)]

[Claim 1] The manufacture approach of the fuel gas which uses as a principal component the hydrogen characterized by carrying out hydrothermal reaction of the liquefied organic substance by supercritical underwater or subcritical underwater one into a reactor.

[Claim 2] The manufacture approach of the fuel gas according to claim 1 which is at least one sort of the slurry which the liquefied organic substance becomes from organic compound content liquid, a solid organic substance crushing object, and water, and the slurry which consists of a solid organic substance crushing object, water, and organic compound content liquid.

[Claim 3] The manufacture approach of fuel gas according to claim 1 that hydrothermal-reaction conditions are liquid linear-velocity (feeding volume / reactor cross section) = 0.1 - 1.0 cm/sec in more than temperature = 200 degree C, more than pressure = 2 MPa-G, and a reactor.

[Claim 4] The manufacture approach of fuel gas according to claim 1 of performing hydrothermal reaction to the bottom of un-existing [of a catalyst] by liquid linear-velocity (feeding volume / reactor cross section) = 0.1 - 1.0 cm/sec in more than temperature = 300 degree C, more than pressure = 10 MPa-G, and a reactor.

[Claim 5] The manufacture approach of fuel gas according to claim 1 of performing hydrothermal reaction to the bottom of existence of a catalyst by liquid linear-velocity (feeding volume / reactor cross section) = 0.1 - 1.0 cm/sec in temperature = 200 degree C, more than pressure = 2 MPa-G, and a reactor.

[Claim 6] The manufacture approach of the fuel gas according to claim 5 which is at least one sort chosen from the group which a catalyst becomes from a titanate-acid compound, zirconia oxide, and a titanium-zirconia multiple oxide.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the approach of manufacturing the fuel gas which uses hydrogen as a principal component by using the liquefied organic substance as a start raw material.

[0002] In this invention, in water, the solid organic substance dissolves or the "liquefied organic substance" means liquefied and/or the liquefied object which distributes and exists.

[0003]

[Description of the Prior Art] the trash (sludge; garbage, such as aerobic treatment sludge, anaerobic treatment sludge, and sludge, --) of the conventional solid organic substance Paper, plastics, a piece of wood, the piece of a bamboo, the piece of grass, straw, fiber, the piece of a vegetable, rubber, a hide, Trash, such as food-processing trash, livestock waste, forest thinning material / fallen tree, and *****, agriculture-and-forestry trash, marine product trash, etc. and a liquefied organic waste (the waste water from a domestic waste, a food-processing factory, etc. --) Waste water, such as waste water from a barn/poultry farm, and industrial waste water with which a biological treatment contains a difficult component; the waste water containing alcohols, carboxylic acids, and aldehydes etc. is processed by the separate technique according to each property.

[0004] In our country, the yield has reached [year] in about 50 million t /only with domestic wastes, and incineration disposal is carried out in many incineration disposal plants the about 75%. However, at such space destroying by fire, it is [whether it is small and] only about 150 places to use trash effectively by power recovery. especially -- recent years -- incineration of various trash -- facing -- the problem that generating of dioxin is big -- becoming -- **** -- continuation of not only construction of a new incineration facility but the operation by a part of existing facility -- it is becoming a difficult situation.

[0005] Sludge is incinerated after dehydration or reclamation processing is more specifically carried out. After activated sludge treatment of the organic substance content waste water is generally carried out, the sludge to generate is destroyed by fire or reclamation processed as mentioned above. Moreover, the trash of the water nature containing the organic substance is incinerated after desiccation as it is.

[0006] However, the yield of a solid organic waste and a liquefied organic waste increases in recent years, and it has been hard coming to cope with it by the approach of carrying out incineration processing of various kinds of trash with the above conventional techniques in the present condition that the regulation on trash is being tightened up by coincidence gradually.

[0007] Moreover, it is also required to reuse these trash as a resource from the view of "a deployment of a limited resource" which is a present big technical technical problem.

[0008]

[Problem(s) to be Solved by the Invention] Therefore, this invention sets it as the main purposes to offer the new technique for collecting and reusing with useful gestalten, such as fuel gas, power, and heat energy, by processing a solid and liquefied organic waste with high gasification efficiency.

[0009]

[Means for Solving the Problem] this invention person found out that the above-mentioned technical problem could be attained mostly, when hydrothermal reaction of these trash was carried out to the bottom of supercritical thru/or a subcritical condition with the gestalt of the liquefied organic substance, as a result of advancing research about the technique of processing a solid and liquefied organic waste, in view of the present condition of the above techniques.

[0010] That is, the approach of manufacturing the fuel gas which this invention uses the following liquefied organic substance as a raw material, and uses hydrogen as a principal component is offered.;

1. Manufacture approach of fuel gas which uses as principal component hydrogen characterized by carrying out hydrothermal reaction of the liquefied organic substance by supercritical underwater or subcritical underwater one into reactor.

2. Manufacture approach of fuel gas given in above-mentioned term 1 which is at least one sort of slurry which the liquefied organic substance becomes from organic compound content liquid, solid organic substance crushing object, and water, and slurry which consists of solid organic substance crushing object, water, and organic compound content liquid.

3. Manufacture approach of fuel gas given in above-mentioned term 1 whose hydrothermal-reaction conditions are liquid linear-velocity (feeding volume / reactor cross section) = 0.1 - 1.0 cm/sec in more than temperature = 200 degree C, more than pressure = 2 MPa-G, and reactor.

4. Manufacture approach of fuel gas given in above-mentioned term 1 which performs hydrothermal reaction to the bottom of un-existing [of a catalyst] by liquid linear-velocity (feeding volume / reactor cross section) = 0.1 - 1.0 cm/sec in more than temperature = 300 degree C, more than pressure = 10 MPa-G, and reactor.

5. Manufacture approach of fuel gas given in above-mentioned term 1 which performs hydrothermal reaction to the bottom of existence of catalyst by liquid linear-velocity (feeding volume / reactor cross section) = 0.1 - 1.0 cm/sec in temperature = 200 degree C, more than pressure = 2 MPa-G, and reactor.

6. Manufacture approach of fuel gas given in above-mentioned term 5 which is at least one sort chosen from group which catalyst becomes from titanite-acid ghost, zirconia oxide, and titanium-zirconia multiple oxide.

[0011]

[Embodiment of the Invention] The liquefied organic substance which this invention makes a processing object includes all the liquefied objects in liquefied and the condition that at least one sort of the solid organic substance is dissolving thru/or distributing, in liquids, such as water.

[0012] Especially the solid organic substance as a source of the organic substance is not limited. Domestic-wastes; aerobic treatment sludge, such as city dust, Sludge, such as anaerobic treatment sludge and sludge; Plants, a bamboo, grass, straw, and fiber the solid organic substance (the shaft of corn --), such as trash of living thing relation, such as vegetable waste, rubber, a hide, and agriculture / forestry / stock raising industry / poultry farming / fisheries, and a product Biomass of the wide sense containing; giant kelps, such as tofu lees, coffee bean-curd refuse, straw, straw, thinning material, and a fallen tree, a eucalyptus, etc.; a mineral product (coal, peat, others) and various kinds of hydrocarbons are illustrated. These solid-like organic substance may be processed by two or more sorts of mixed state.

[0013] The domestic waste which contains garbage, paper, plastics, etc. as a liquefied source of the organic substance, The waste water containing organic compounds, such as alcohols, carboxylic acids, and aldehydes, Nightsoil, plating waste water, food industrial waste water, paper mill waste water, pharmaceutical factory waste water, photograph waste water, The waste water containing the organic substance, such as waste water generated with liquefaction or gasification of printing waste water, agricultural-chemicals related waste water, dyeing waste water, semiconductor manufacture industrial waste water, and coal and waste water generated in connection with the pyrolysis of city dust, etc. is illustrated.

[0014] The above-mentioned shape of a solid and the above-mentioned liquefied source of the organic substance usually contain one sort of metal components, such as Mg, aluminum, Si, P, calcium, Ti, Cr, Mn, Fe, Co, nickel, Cu, Zn, and Cd, or two sorts or more. this invention approach

can be enforced even if the processed material contains such a metal component.

[0015] The liquefied organic substance which this invention makes a processing object can be formed by adding and stirring liquids, such as water, if needed to at least one sort of the above shape of a solid, and the liquefied source of the organic substance. Under the present circumstances, since the source of the solid-like organic substance makes a slurry form, grinding in suitable magnitude beforehand is desirable.

[0016] The invention in this application is explained to a detail, referring to a drawing below.

[0017] Drawing 1 is a flow sheet which shows the outline of the invention-in-this-application approach.

[0018] In order to remove inorganic machine components, such as a metal and glass, as much as possible if needed, after judgment processing is carried out and being sent subsequently to a rough crusher with a pre-treatment equipment (not shown) according to a conventional method, with water and/or the liquefied source of the organic substance, organic waste objects, such as organic compound content trash and biomass, are sent to the reservoir tank 1, and are stored as the liquefied organic substance thru/or a solid organic substance slurry.

[0019] In this invention, the liquefied organic substance formed as mentioned above is processed as shown in drawing 1. That is, after the liquefied organic substance held in the reservoir tank 1 is heated by the temperature of 200 degrees C or more by the heat exchanger 5 through a pump 3, it is supplied to the hydrothermal reactor 7 and solubilization and gasification are presented with it.

[0020] The heating means of arbitration can be used as the above-mentioned source of heating. for example, hydrothermal reaction -- a column -- heating with a heater (not shown), when heat exchange is performed in the vapor-liquid mixing phase and heat exchanger 5 from an outlet or predetermined reaction temperature cannot be maintained at the time of hydrothermal reaction, or when you need the temperature up to predetermined temperature **** -- or the hydrothermal reaction from a steam generator (not shown) -- a steam can also be supplied to a column 7. Moreover, also in order to make temperature in the hydrothermal-reaction column 7 into predetermined temperature on the occasion of a start-up, the temperature up of the open steam can be fed and carried out into a hydrothermal reactor, or the temperature up of the heater (not shown) can also be formed and carried out between a heat exchanger and a hydrothermal reactor.

[0021] In addition, water, waste water, etc. may be added from a tank 9 to the liquefied organic substance through a pump 11 for concentration adjustment of the liquefied organic substance. The reaction in the hydrothermal reactor 7 is performed under supercritical thru/or a subcritical condition to the bottom of existence of a catalyst or un-existing. the temperature and the pressure in hydrothermal reaction -- use of a catalyst -- or -- un--- although determined according to the presentation of the liquefied organic substance used and processed etc., it is usually within the limits of the temperature of about 200-600 degrees C, and a pressure 2 - 50MPa extent. so that the temperature and/or the pressure at the time of hydrothermal reaction are high -- the cracking severity of the organic substance -- rising -- moreover, hydrothermal reaction -- what is necessary is just to define the temperature and the pressure at the time of hydrothermal reaction synthetically in consideration of the pollutants concentration in the liquefied organic substance, running cost, a construction cost, etc., since an installation cost increases on the other hand although the residence time of the processed material (liquefied organic substance) in a column 7 is also shortened When performing hydrothermal reaction to the bottom of un-existing [of a catalyst], temperature is [10 or more (preferably 15 or more MPas) MPas and the linear velocity of 300 degrees C or more (preferably 350 degrees C or more) and a pressure] usually 0.1 - 1.0 cm/sec extent.

[0022] When performing hydrothermal reaction to the bottom of existence of a catalyst, temperature is [2 or more (preferably 5 or more MPas) MPas and the linear velocity of 200 degrees C or more (preferably 250 degrees C or more) and a pressure] usually 0.1 - 1.0 cm/sec extent.

[0023] In this invention, since hydrothermal reaction is promoted when using a catalyst, the cracking severity of the organic component in the liquefied organic substance improves.

Therefore, under certain hydrothermal-reaction conditions, miniaturizing hydrothermal-reaction equipment and/or reaction time can be shortened. Or when using the hydrothermal-reaction equipment of the same volume, shortening reaction time and/or a mild reaction condition can be adopted.

[0024] The thing which was chosen from the group which consists of mixture of the zirconic acid ghost excellent in endurance, titanium oxide, and a zirconic acid ghost and titanium oxide and a zirconia-titania multiple oxide as a catalyst and which use a kind at least is desirable.

[0025] Especially the configuration of a catalyst is not limited but the shape of the shape of a globular shape, a pellet type, cylindrical, and a spall, powder, and a honeycomb etc. is illustrated. the hydrothermal reaction in the case of carrying out restoration use of such a support catalyst -- the volume of a column 7 -- the case of the fixed bed -- the space velocity (inlet-port criteria) of liquid -- 0.5 - 100hr- it is [about one] good to make it become about 1-60hr-1 more preferably. In the case of the shape of the shape of a globular shape, a pellet type, cylindrical, and a spall, and powder etc., the magnitude of the support catalyst used by the fixed bed is usually about 5-15mm more preferably about 1-20mm. Moreover, as a honeycomb structure object in the case of supporting and using a catalyst for honeycomb-like support, the thing of a square, a hexagon, and the configuration of which circular arbitration is used for opening. Although the area per unit volume, especially a numerical aperture, etc. are not limited, 200-800m²/m³ and the thing of about 40 - 80% of numerical apertures are usually used as an area per unit volume. The zirconia, titania, and titania-zirconia which was excellent in endurance also as the quality of the material of a honeycomb structure object is more desirable.

[0026] hydrothermal reaction -- the amount in which a catalyst can form the fluid bed within a reactor when making the fluid bed form in a column 7 -- that is, on the basis of the weight of the liquid phase, the liquid phase is made to suspend about 0.1 - 3% in the shape of a slurry, and it is usually used more preferably about 0.01 to 10%. the condition of having made the catalyst suspending in the shape of a slurry in the liquid phase when adopting the fluid bed -- hydrothermal reaction -- a column 7 is supplied, from the liquid phase discharged out of the reactor after reaction termination, separation recovery is carried out by suitable approaches, such as sedimentation and centrifugal separation, and the reuse of the catalyst is carried out. Therefore, if the ease of separation recovery of the catalyst from the liquid phase is taken into consideration, as for the particle size of the catalyst used in the fluid bed, it is more desirable to be referred to as about 0.15-0.5mm. Within the hydrothermal reactor 7, the organic substance solubilizes, and since it liquefies and the concentration of an inorganic substance increases relatively, it discharges out of a hydrothermal reactor by making this into a sludge. namely, hydrothermal reaction -- the bulb between the sludge exhausts (; which is not illustrated -- it may only be called the "exhaust" below) by which the pressure up was carried out to a column and this ** -- opening -- a sludge -- hydrothermal reaction -- the exhaust is made to sediment from a column 10 When a sludge fully sediments, the above-mentioned bulb is closed, after carrying out natural temperature fall **** pressure lowering, the bulb prepared in the exhaust outlet side is opened, and sludge liquid is discharged out of a system. Moreover, since metaled solubility decreases sharply by performing hydrothermal-reaction processing under supercritical conditions, desludging can be efficiently performed in this phase.

[0027] Well-known solid-liquid-separation processing can be presented with sludge liquid, and a supernatant liquid can be circulated through and processed on the reservoir tank 1. With such a lock hopper method, the sludge generated within the hydrothermal reactor 7 can be extracted semi-continuously, and can be discharged. Moreover, the metal component in solubilization liquid is removable with well-known technique, such as coagulation sedimentation. hydrothermal reaction -- by removal of the sludge generated in the column, and/or a metal component, a deposit/adhesion of the sludge in a consecutive waste-water-treatment system and/or a metal component can be controlled, and a waste-water-treatment system can be managed easily.

[0028] Subsequently in a cooling system 15, vapor liquid separation of the vapor-liquid mixing phase formed by the hydrothermal reactor 7 is carried out to the gas (gaseous phase) and reaction mixture (liquid phase) which use hydrogen as a principal component. By this cooling and vapor-liquid-separation actuation, most impurities in a raw material other than a sulfur

compound shift to a liquid phase side.

[0029] Through the dwelling valve 17, the gas which uses hydrogen as a principal component is taken out of a system, and is acquired as a product. The sulfur component contained in the liquefied organic substance which is a start raw material reacts with the hydrogen generated by hydrothermal reaction, and forms H₂S. These H₂S are removable by presenting the desulfurization actuation (for example, desulfurization actuation which uses adsorption material, such as ZnS) by the conventional method with the gas which uses hydrogen as a principal component.

[0030] On the other hand, if required, after heat recovery is carried out, according to a conventional method, the waste water treatment of the separated liquid phase will be carried out. Moreover, this liquid phase can also be used as a dilution water of a solid organic substance crushing object.

[0031] Moreover, if required, after power recovery is carried out by an expansion turbine (or reciprocation type power recovery system) etc. according to a conventional method, a decarboxylation will be presented with high-pressure gas by means, such as PSA, separation transparency film, or a lye scrubbing tower, and it will be collected as hydrogen-rich gas.

[0032] Furthermore, periodically, acid water solutions (a nitric acid, ascorbic acid, etc.) and/or an alkali water solution can wash the internal surface of piping used by this invention approach, and an equipment, or an air wash can also be carried out if needed.

[0033]

[Effect of the Invention] Since the solid organic substance (trash and biomass) and/or the solid liquefied organic substance can be transformed to the fuel gas which uses useful hydrogen as a principal component by the high energy conversion efficiency according to this invention approach, the manufacturing cost of fuel gas is reduced remarkably.

[0034] Moreover, since the amount of the fossil fuel used is reducible while contributing to diversification of the fuel gas manufacture source by reusing as a resource various kinds of trash generated in large quantities according to this invention approach, it can contribute to maintenance of earth environment greatly.

[0035] furthermore -- since generating of harmful matter, such as dioxin which was the greatest trouble of the waste treatment by the conventional technique, can be prevented effectively according to this invention approach -- environmental pollution, such as atmospheric air and soil, -- substantial -- a dissolution -- or it is remarkably mitigable.

[0036] According to this invention approach, as compared with the waste treatment approach which is mainly concerned with the conventional incineration disposal, power, heat energy, etc. can be collected more efficiently and in large quantities further again.

[0037] Furthermore, into the gaseous phase after carrying out vapor liquid separation of the hydrothermal reactor outlet product, existence of an injurious ingredient is not accepted substantially.

[0038] Moreover, the sludge formed by the hydrothermal reactor is excellent in sedimentation nature, and the removal from equipment and handling are easy for it.

[0039]

[Example] An example is shown below and the place by which it is characterized [of this invention] is clarified further.

According to the flow shown in example 1 drawing 1, the liquefied organic substance (methanol 50% content water) was processed under un-existing [of a catalyst] by the invention-in-this-application approach.

[0040] That is, the liquefied organic substance was supplied to the hydrothermal reactor 7 by space-velocity 3hr⁻¹, and supercritical hydrothermal reaction was performed to the bottom of the condition shown in the following table 1. hydrothermal-reaction-izing -- the liquid linear velocity in a column 7 was 0.5 cm/sec. Table 1 shows the rate of methanolysis, the amount of gas generation, a gas presentation, etc. collectively.

Hydrothermal reaction of methanol content water was performed like the example 1 of reference except having been filled up with TiO₂ catalyst with a particle size of 2mm in the example 2 hydrothermal reactor 7. A result is collectively shown in Table 1.

Hydrothermal reaction of methanol content water was performed like the example 1 of reference except having been filled up with Ru2%-TiO₂ catalyst with a particle size of 2mm in the example of reference 1 hydrothermal reactor 7. A result is collectively shown in Table 1.

[0041]

[Table 1]

	実施例 1	実施例 2	参考例 1
反応塔内容積(cc)	1 0 0	1 0 0	1 0 0
充填物	なし	TiO ₂ 触媒	Ru-TiO ₂ 触媒
温度(℃)	4 7 0	4 7 0	4 0 0
圧力(MPa)	2 5	2 5	2 5
CH ₃ OH 含有水流量 (l/hr)	0. 0 8	0. 3 8	0. 4 4
CH ₃ OH 分解率 (%)	1 0 0	1 0 0	1 0 0
ガス発生量 (Nl/hr)	6 3	2 1 3	3 5 2
H ₂ (%)	5 8	5 0	6 4
CH ₄ (%)	3	2 2	5
CO(%)	2 6	3	3
CO ₂ (%)	2	2 5	2 3

[0042] According to this invention hydrothermal-reaction approach, the fuel gas which has the gas presentation near the hydrothermal reaction under existence of Ru-TiO₂ catalyst is obtained so that clearly from the result shown in Table 1.

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TECHNICAL FIELD

[Field of the Invention] This invention relates to the approach of manufacturing the fuel gas which uses hydrogen as a principal component by using the liquefied organic substance as a start raw material.

[0002] In this invention, in water, the solid organic substance dissolves or the "liquefied organic substance" means liquefied and/or the liquefied object which distributes and exists.

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EFFECT OF THE INVENTION

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MEANS

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[0010] That is, the approach of manufacturing the fuel gas which this invention uses the following liquefied organic substance as a raw material, and uses hydrogen as a principal component is offered.;

1. Manufacture approach of fuel gas which uses as principal component hydrogen characterized by carrying out hydrothermal reaction of the liquefied organic substance by supercritical underwater or subcritical underwater one into reactor.
2. Manufacture approach of fuel gas given in above-mentioned term 1 which is at least one sort of slurry which the liquefied organic substance becomes from organic compound content liquid, solid organic substance crushing object, and water, and slurry which consists of solid organic substance crushing object, water, and organic compound content liquid.
3. Manufacture approach of fuel gas given in above-mentioned term 1 whose hydrothermal-reaction conditions are liquid linear-velocity (feeding volume / reactor cross section) = 0.1 - 1.0 cm/sec in more than temperature = 200 degree C, more than pressure = 2 MPa-G, and reactor.
4. Manufacture approach of fuel gas given in above-mentioned term 1 which performs hydrothermal reaction to the bottom of un-existing [of a catalyst] by liquid linear-velocity (feeding volume / reactor cross section) = 0.1 - 1.0 cm/sec in more than temperature = 300 degree C, more than pressure = 10 MPa-G, and reactor.
5. Manufacture approach of fuel gas given in above-mentioned term 1 which performs hydrothermal reaction to the bottom of existence of catalyst by liquid linear-velocity (feeding volume / reactor cross section) = 0.1 - 1.0 cm/sec in temperature = 200 degree C, more than pressure = 2 MPa-G, and reactor.
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[0012] Especially the solid organic substance as a source of the organic substance is not limited. Domestic-wastes; aerobic treatment sludge, such as city dust, Sludge, such as anaerobic treatment sludge and sludge; Plants, a bamboo, grass, straw, and fiber the solid organic substance (the shaft of corn --), such as trash of living thing relation, such as vegetable waste, rubber, a hide, and agriculture / forestry / stock raising industry / poultry farming / fisheries, and a product Biomass of the wide sense containing; giant kelps, such as tofu lees, coffee bean-curd refuse, straw, straw, thinning material, and a fallen tree, a eucalyptus, etc.; a mineral product (coal, peat, others) and various kinds of hydrocarbons are illustrated. These solid-like

organic substance may be processed by two or more sorts of mixed state.

[0013] The domestic waste which contains garbage, paper, plastics, etc. as a liquefied source of the organic substance, The waste water containing organic compounds, such as alcohols, carboxylic acids, and aldehydes, Nightsoil, plating waste water, food industrial waste water, paper mill waste water, pharmaceutical factory waste water, photograph waste water, The waste water containing the organic substance, such as waste water generated with liquefaction or gasification of printing waste water, agricultural-chemicals related waste water, dyeing waste water, semiconductor manufacture industrial waste water, and coal and waste water generated in connection with the pyrolysis of city dust, etc. is illustrated.

[0014] The above-mentioned shape of a solid and the above-mentioned liquefied source of the organic substance usually contain one sort of metal components, such as Mg, aluminum, Si, P, calcium, Ti, Cr, Mn, Fe, Co, nickel, Cu, Zn, and Cd, or two sorts or more. this invention approach can be enforced even if the processed material contains such a metal component.

[0015] The liquefied organic substance which this invention makes a processing object can be formed by adding and stirring liquids, such as water, if needed to at least one sort of the above shape of a solid, and the liquefied source of the organic substance. Under the present circumstances, since the source of the solid-like organic substance makes a slurry form, grinding in suitable magnitude beforehand is desirable.

[0016] The invention in this application is explained to a detail, referring to a drawing below.

[0017] Drawing 1 is a flow sheet which shows the outline of the invention-in-this-application approach.

[0018] In order to remove inorganic machine components, such as a metal and glass, as much as possible if needed, after judgment processing is carried out and being sent subsequently to a rough crusher with a pre-treatment equipment (not shown) according to a conventional method, with water and/or the liquefied source of the organic substance, organic waste objects, such as organic compound content trash and biomass, are sent to the reservoir tank 1, and are stored as the liquefied organic substance thru/or a solid organic substance slurry.

[0019] In this invention, the liquefied organic substance formed as mentioned above is processed as shown in drawing 1. That is, after the liquefied organic substance held in the reservoir tank 1 is heated by the temperature of 200 degrees C or more by the heat exchanger 5 through a pump 3, it is supplied to the hydrothermal reactor 7 and solubilization and gasification are presented with it.

[0020] The heating means of arbitration can be used as the above-mentioned source of heating. for example, hydrothermal reaction -- a column -- heating with a heater (not shown), when heat exchange is performed in the vapor-liquid mixing phase and heat exchanger 5 from an outlet or predetermined reaction temperature cannot be maintained at the time of hydrothermal reaction, or when you need the temperature up to predetermined temperature **** -- or the hydrothermal reaction from a steam generator (not shown) -- a steam can also be supplied to a column 7. Moreover, also in order to make temperature in the hydrothermal-reaction column 7 into predetermined temperature on the occasion of a start-up, the temperature up of the open steam can be fed and carried out into a hydrothermal reactor, or the temperature up of the heater (not shown) can also be formed and carried out between a heat exchanger and a hydrothermal reactor.

[0021] In addition, water, waste water, etc. may be added from a tank 9 to the liquefied organic substance through a pump 11 for concentration adjustment of the liquefied organic substance. The reaction in the hydrothermal reactor 7 is performed under supercritical thru/or a subcritical condition to the bottom of existence of a catalyst or un-existing. the temperature and the pressure in hydrothermal reaction -- use of a catalyst -- or -- un--- although determined according to the presentation of the liquefied organic substance used and processed etc., it is usually within the limits of the temperature of about 200-600 degrees C, and a pressure 2 - 50MPa extent. so that the temperature and/or the pressure at the time of hydrothermal reaction are high -- the cracking severity of the organic substance -- rising -- moreover, hydrothermal reaction -- what is necessary is just to define the temperature and the pressure at the time of hydrothermal reaction synthetically in consideration of the pollutants concentration in the

liquefied organic substance, running cost, a construction cost, etc., since an installation cost increases on the other hand although the residence time of the processed material (liquefied organic substance) in a column 7 is also shortened When performing hydrothermal reaction to the bottom of un-existing [of a catalyst], temperature is [10 or more (preferably 15 or more MPas) MPas and the linear velocity of 300 degrees C or more (preferably 350 degrees C or more) and a pressure] usually 0.1 – 1.0 cm/sec extent.

[0022] When performing hydrothermal reaction to the bottom of existence of a catalyst, temperature is [2 or more (preferably 5 or more MPas) MPas and the linear velocity of 200 degrees C or more (preferably 250 degrees C or more) and a pressure] usually 0.1 – 1.0 cm/sec extent.

[0023] In this invention, since hydrothermal reaction is promoted when using a catalyst, the cracking severity of the organic component in the liquefied organic substance improves. Therefore, under certain hydrothermal-reaction conditions, miniaturizing hydrothermal-reaction equipment and/or reaction time can be shortened. Or when using the hydrothermal-reaction equipment of the same volume, shortening reaction time and/or a mild reaction condition can be adopted.

[0024] The thing which was chosen from the group which consists of mixture of the zirconic acid ghost excellent in endurance, titanium oxide, and a zirconic acid ghost and titanium oxide and a zirconia-titania multiple oxide as a catalyst and which use a kind at least is desirable.

[0025] Especially the configuration of a catalyst is not limited but the shape of the shape of a globular shape, a pellet type, cylindrical, and a spall, powder, and a honeycomb etc. is illustrated. the hydrothermal reaction in the case of carrying out restoration use of such a support catalyst -- the volume of a column 7 -- the case of the fixed bed -- the space velocity (inlet-port criteria) of liquid -- 0.5 – 100hr- it is [about one] good to make it become about 1-60hr-1 more preferably. In the case of the shape of the shape of a globular shape, a pellet type, cylindrical, and a spall, and powder etc., the magnitude of the support catalyst used by the fixed bed is usually about 5-15mm more preferably about 1-20mm. Moreover, as a honeycomb structure object in the case of supporting and using a catalyst for honeycomb-like support, the thing of a square, a hexagon, and the configuration of which circular arbitration is used for opening. Although the area per unit volume, especially a numerical aperture, etc. are not limited, 200-800m²/m³ and the thing of about 40 – 80% of numerical apertures are usually used as an area per unit volume. The zirconia, titania, and titania-zirconia which was excellent in endurance also as the quality of the material of a honeycomb structure object is more desirable.

[0026] hydrothermal reaction -- the amount in which a catalyst can form the fluid bed within a reactor when making the fluid bed form in a column 7 -- that is, on the basis of the weight of the liquid phase, the liquid phase is made to suspend about 0.1 – 3% in the shape of a slurry, and it is usually used more preferably about 0.01 to 10%. the condition of having made the catalyst suspending in the shape of a slurry in the liquid phase when adopting the fluid bed -- hydrothermal reaction -- a column 7 is supplied, from the liquid phase discharged out of the reactor after reaction termination, separation recovery is carried out by suitable approaches, such as sedimentation and centrifugal separation, and the reuse of the catalyst is carried out. Therefore, if the ease of separation recovery of the catalyst from the liquid phase is taken into consideration, as for the particle size of the catalyst used in the fluid bed, it is more desirable to be referred to as about 0.15-0.5mm. Within the hydrothermal reactor 7, the organic substance solubilizes, and since it liquefies and the concentration of an inorganic substance increases relatively, it discharges out of a hydrothermal reactor by making this into a sludge. namely, hydrothermal reaction -- the bulb between the sludge exhausts (; which is not illustrated -- it may only be called the "exhaust" below) by which the pressure up was carried out to a column and this ** -- opening -- a sludge -- hydrothermal reaction -- the exhaust is made to sediment from a column 10 When a sludge fully sediments, the above-mentioned bulb is closed, after carrying out natural temperature fall **** pressure lowering, the bulb prepared in the exhaust outlet side is opened, and sludge liquid is discharged out of a system. Moreover, since metaled solubility decreases sharply by performing hydrothermal-reaction processing under supercritical conditions, desludging can be efficiently performed in this phase.

[0027] Well-known solid-liquid-separation processing can be presented with sludge liquid, and a supernatant liquid can be circulated through and processed on the reservoir tank 1. With such a lock hopper method, the sludge generated within the hydrothermal reactor 7 can be extracted semi-continuously, and can be discharged. Moreover, the metal component in solubilization liquid is removable with well-known technique, such as coagulation sedimentation. hydrothermal reaction -- by removal of the sludge generated in the column, and/or a metal component, a deposit/adhesion of the sludge in a consecutive waste-water-treatment system and/or a metal component can be controlled, and a waste-water-treatment system can be managed easily.

[0028] Subsequently in a cooling system 15, vapor liquid separation of the vapor-liquid mixing phase formed by the hydrothermal reactor 7 is carried out to the gas (gaseous phase) and reaction mixture (liquid phase) which use hydrogen as a principal component. By this cooling and vapor-liquid-separation actuation, most impurities in a raw material other than a sulfur compound shift to a liquid phase side.

[0029] Through the dwelling valve 17, the gas which uses hydrogen as a principal component is taken out out of a system, and is acquired as a product. The sulfur component contained in the liquefied organic substance which is a start raw material reacts with the hydrogen generated by hydrothermal reaction, and forms H₂S. These H₂S are removable by presenting the desulfurization actuation (for example, desulfurization actuation which uses adsorption material, such as ZnS) by the conventional method with the gas which uses hydrogen as a principal component.

[0030] On the other hand, if required, after heat recovery is carried out, according to a conventional method, the waste water treatment of the separated liquid phase will be carried out. Moreover, this liquid phase can also be used as a dilution water of a solid organic substance crushing object.

[0031] Moreover, if required, after power recovery is carried out by an expansion turbine (or reciprocation type power recovery system) etc. according to a conventional method, a decarboxylation will be presented with high-pressure gas by means, such as PSA, separation transparency film, or a lye scrubbing tower, and it will be collected as hydeogen-rich gas.

[0032] Furthermore, periodically, acid water solutions (a nitric acid, ascorbic acid, etc.) and/or an alkali water solution can wash the internal surface of piping used by this invention approach, and an equipment, or an air wash can also be carried out if needed.

[Translation done.]

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EXAMPLE

[Example] An example is shown below and the place by which it is characterized [of this invention] is clarified further.

According to the flow shown in example 1 drawing 1 , the liquefied organic substance (methanol 50% content water) was processed under un-existing [of a catalyst] by the invention-in-this-application approach.

[0040] That is, the liquefied organic substance was supplied to the hydrothermal reactor 7 by space-velocity 3hr⁻¹, and supercritical hydrothermal reaction was performed to the bottom of the condition shown in the following table 1. hydrothermal-reaction-izing -- the liquid linear velocity in a column 7 was 0.5 cm/sec. Table 1 shows the rate of methanolysis, the amount of gas generation, a gas presentation, etc. collectively.

Hydrothermal reaction of methanol content water was performed like the example 1 of reference except having been filled up with TiO₂ catalyst with a particle size of 2mm in the example 2 hydrothermal reactor 7. A result is collectively shown in Table 1.

Hydrothermal reaction of methanol content water was performed like the example 1 of reference except having been filled up with Ru2%-TiO₂ catalyst with a particle size of 2mm in the example of reference 1 hydrothermal reactor 7. A result is collectively shown in Table 1.

[0041]

[Table 1]

	実施例 1	実施例 2	参考例 1
反応塔内容積(cc)	1 0 0	1 0 0	1 0 0
充填物	なし	TiO ₂ 触媒	Ru-TiO ₂ 触媒
温度(℃)	4 7 0	4 7 0	4 0 0
圧力(MPa)	2 5	2 5	2 5
CH ₃ OH 含有水流量 (l/hr)	0. 0 8	0. 3 8	0. 4 4
CH ₃ OH 分解率 (%)	1 0 0	1 0 0	1 0 0
ガス発生量 (Nl/hr)	6 3	2 1 3	3 5 2
H ₂ (%)	5 8	5 0	6 4
CH ₄ (%)	3	2 2	5
CO(%)	2 6	3	3
CO ₂ (%)	2	2 5	2 3

[0042] According to this invention hydrothermal-reaction approach, the fuel gas which has the gas presentation near the hydrothermal reaction under existence of Ru-TiO₂ catalyst is obtained so that clearly from the result shown in Table 1.

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DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] It is the flow sheet which shows the outline of this invention.

[Description of Notations]

- 1 -- Reservoir tank
- 3 -- Pump
- 5 -- Heat exchanger
- 7 -- Hydrothermal reactor
- 9 -- Water tank
- 11 -- Pump
- 13 -- Condensator
- 15 -- Vapor-liquid-separation machine
- 17 -- Dwelling valve
- 19 -- Level regulating valve

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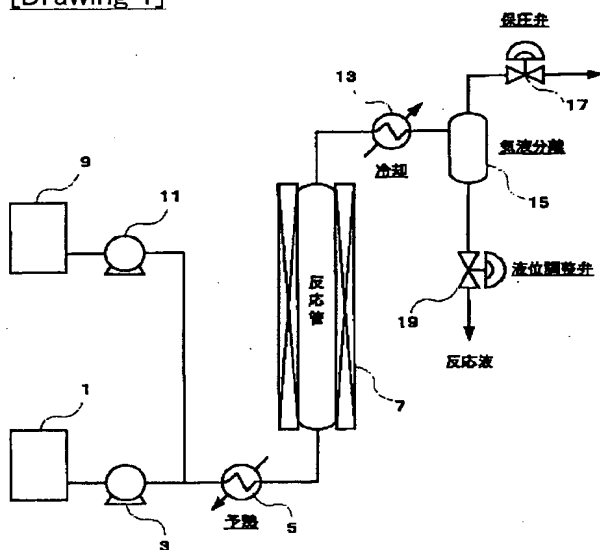
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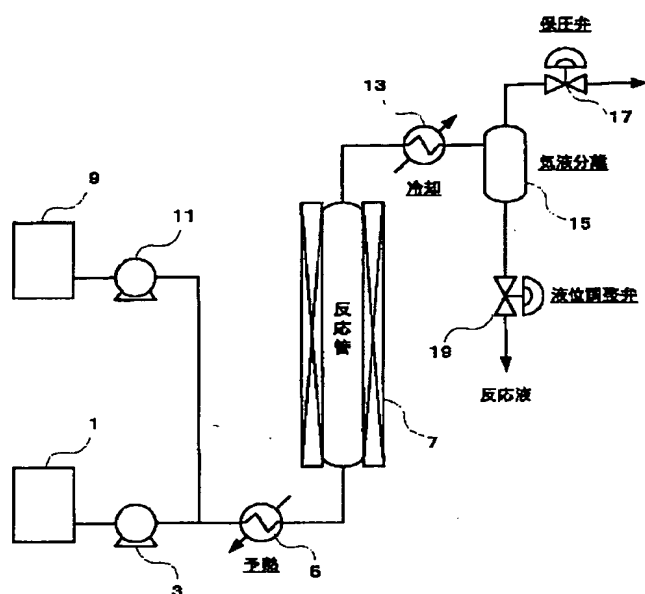
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DRAWINGS

[Drawing 1]



[Translation done.]

Drawing selection Representative drawing

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